ADIABATIC INITIATION SENSITIVITY OF LIQUID ENERGETIC MATERIALS

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ABSTRACT

Adiabatic compression sensitivity analysis and test methods were evaluated to determine safety in pumped liquid/slurry processes. Several energetic liquids were evaluated. Pumping conditions and loads were determined for safe transport of liquids, based on analysis and test results.

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ADIABATIC COMPRESSION

Numerous explosive processing operations require pumping of liquid and slurry energetic material. If the liquids/slurries have high vapor pressure or have vapors entrapped in them, a potential for adiabatic compression initiation at pumps exists. In this paper, a method for evaluating the initiation potential is presented. In addition, examples of liquid materials that can be initiated are illustrated.

BASIC HAZARDS DEFINITION

Ignition hazards exist in liquid or slurry materials during transport if they are energetic and are subject to sudden compression loading. The reaction may result in high output (explosion) once heat is generated as a result of ignition. Hazardous conditions may occur if one or more of the following exists in the liquid/slurry:

- Material is energetic and capable of explosion or detonation
- Material has vapor bubbles in it
- Material has air trapped in it
- Material is sensitive to heat, impact and adiabatic compression.

When liquid/slurry is transported under pressure or subject to gravity fall in a given system, the system should be designed to prevent initiation due to adiabatic compression. Excessive pressures developed in the process can create very high localized temperatures in vapor bubbles to ignite the fluid. There are many sources of excessive pressure; wherein, one or more are present in the field handling system. The pressures commonly referred to as ‘surge pressures" are as follows:

- Pressure waves caused by opening a valve between high pressure and low pressure domain
- Pressure surges produced by the application of external static load
- Pressure surges caused by deceleration of moving masses
- Pressure waves related to pump characteristics commonly referred to as "pump ripple"

- Rapid compression of gas bubble in contact with liquid force due to mechanical shock in a pump

- Rapid compression of a gas bubble in a pump

Pressure waves produced by the opening of a valve between high pressure and low pressure can be expressed as:

$P_{max}/\Delta P$ = maximum pressure at peak/applied pressure differential = 2

For static load, the pressure surge can be determined from:

$$P_{max} = W/A$$

where: W = applied load
A = piston area supported by fluid

Pressure surges produced by the deceleration of moving masses are described by the relationship:

$$\Delta P = mv^2E/Vg$$

where: ΔP = excess pressure produced
m = weight being decelerated
v = velocity at which the weight moves
E = bulk modulus of the fluid
V = volume of fluid being compressed
g = acceleration due to gravity

ADIABATIC COMPRESSION MECHANISM

If a gas bubble should exist in the fluid in a pump, its compression will result in a high temperature in the collapsed bubble as follows:

Adiabatic Conditions

$$\left(\frac{T_F}{T_o}\right)^{\frac{n}{n-1}} = \left(\frac{V_o}{V_F}\right)^{n} = \frac{P_F}{P_o}$$

where:
P = Pressure (psi)
V = Volume (m^3)
T = Temperature (^0C)
n = Polytropic Exponent
subscripts

o = Initial Conditions
f = Final Conditions

Energy in compression assuming it to be adiabatic is:

$$W = \frac{P_o V_o}{\gamma - 1} \left[1 - \left(\frac{P_F}{P_0} \right)^{\frac{\gamma-1}{\gamma}} \right]$$

For ideal gas $\left(\frac{P_F}{P_o} \right)^{\frac{\gamma-1}{\gamma}} = \frac{T_F}{T_o}$

and $P_o V_o = n_g R_o T_o$

then $W = \frac{P_o V_o}{r-1} \left(1 - \frac{T_F}{T_o} \right)$

IN PROCESS POTENTIALS

In diaphragm pumps, check valves are utilized to permit positive displacement of liquids and slurries. As one diaphragm side is activated by air pressure, the other side usually is drawing liquid slurry into it for explosion later. If an air or vapor bubble should be present in the fluid, it would collapse under compression to develop high temperatures in the fluid. If compression was high enough, fluid initiation could occur. Typical pump characteristics are show in Table 1. The impact/compression energy to the fluid can be estimated as follows:

$$E_A = \frac{Horsepower \times Efficiency \times Corrections\ Factor}{Liquid\ Flow\ (\dot{V})}$$

$$E_A = \frac{Horsepower \times 0.8 \times 746.7}{\dot{V}}$$

where:
HP = Motor Horsepower
$\dot{V}$ = Liquid Flow Rate m^3/s
E_A = $Joule/m^3$

For example: Pump A from Table 1.

HP = 0.5

Chamber Volume

$$\dot{V} = 227\ cm^3$$

Strokes/min. = 180

$$\dot{V} = 681 \times 10^{-6}\ m^3/s$$

and Energy/Volume is:

$$E_A = 0.4 \times 39 \times 10^{+6}\ J/m^3$$

The compression power applied to a theoretical gas bubble can be calculated as follows:

$$P_c = \frac{0.8 \times HP \times 746.7}{(5\%\ \text{of chamber volume})}$$

For our example:

Chamber Volume = 227 cm^3
HP = 0.5

then

$$P_c = 26.3 \times 10^6\ J/m^3\text{-sec}$$

The adiabatic temperature rise in a pump can be calculated as follows:

$$\left(\frac{T_F}{T_1}\right) = \left(\frac{P_F}{P_o}\right)^{\frac{\gamma - 1}{\gamma}}$$

For our case let y = 1.4

P_F = 225 psig
= 239.7 psia
P_o = 14.7 psia

then

$$\frac{T_F}{T_1} = 2.22$$

for initial temperature of

T_1 = 100 ^oF
= 560 ^oR

TABLE I

TYPICAL DIAPHRAGM PUMP CHARACTERISTICS AND IN-PROCESS POTENTIALS

Nominal (1 to 2 gpm)

Characteristic	Pump (A)	Pump (B)	Pump (C)
1. Maximum Capacity $\frac{\text{Gallons}}{\text{Hour}}$	144	114	260
2. Maximum Discharge Pressure (psig)	225	60	500
3. Motor Horsepower	1/2	1/2	1
4. Chamber Volume (cm^3)	227	100	180.3
5. Strokes per Minute	180	142	116
6. Compression Ratio	1.286	2.026	4.635
7. Compression Power Applied to Theoretical Gas Bubble (Max.) (Joules/m^3sec)	26.3×10^6	59.7×10^6	66.3×10^6

then

$$T_2 = 772\ {}^0F$$

The compression ratio in the pump is determined based on the following:

$$CR = \frac{Chamber\ Volume}{Chamber\ Volume - Fluid\ Discharge / Stroke}$$

For our case

$$V_c = 227\ cm^3$$

$$Q \text{ (Liquid Discharge/Stroke)} = \frac{144\ gal/hr}{60\ \min/hr} \text{x } 3785 \frac{cm^3}{gal} / \ 180 strokes/\min$$

$$Q = 50.47\ cm^3/\text{stroke}$$

then

$$CR = \frac{227}{227-50.47}$$

$$CR = 1.286$$

Check valve adiabatic energy/volume due to pulsations can be calculated as follows:

$$E_{CC} = \frac{P\max \times A_{ball} \times L}{A_, x \mathrm{T}_{Fl}}$$

where:

P_{max} = Max discharge pressure
A_{ball} = Ball or disk area
L = Ball distance of travel
A_s = Area of seat
T_{FL} = Assumed fluid thickness 0.005 cm

For Pump C

P_{max} = 500 psi
A_{ball} = 0.60 in^2
A_s = 1.12 cm^2
L = 0.219 in

$$E_{CC} = \frac{(500\ lb/in^2) \times (0.60 in^2) \times (.219 inch) \frac{1}{12} \times 1.3558 \frac{J}{FT^3}}{(1.12 cm^2) \times (0.005 cm) \times 10^{-6}\ m^3/cm^3}$$

$$E_{CC} = 1325 \times 10^6\ J/m^3$$

In process potential calculations for 3 types of diaphragm pumps were made and are show in Table II.

TABLE II

IN-PROCESS POTENTIALS - PUMPS

CHARACTERISTIC	PUMP (A)	PUMP (B)	PUMP (C)
1. Energy to Liquid in Chamber (Max) (J/m^3)	0.44×10^6	1.3×10^6	1.71×10^6
2. Compression Power Applied to Theoretical Gas Bubble (Max) (J/m^3 sec)	26×10^6	60×10^6	66×10^6
3. Theoretical Adiabatic Temperature (At Max Pressure) (^0F)	772^0	431^0	1086^0
4. Compression Ratio (Max to Min Chamber Volume)	1.227	2.073	4.509
5. Water Hammer Overpressure (Max) (Psi)	284.5	284.5	244.7
6. Check Valve Energy (Max) (J/m^3)	839×10^6	677×10^6	1323×10^6

LIQUID/SLURRY CHARACTERIZATIONS - TESTS AND EVALUATION

Rapid compression can result from mechanical shock to containers of fuel, or from rapid closing of valves (as described above) in propellant lines containing entrained gas bubbles. Such phenomena are thought to be responsible for a number of accidental explosions. Therefore, sensitivity of liquid materials to the initiation of decomposition in the presence of rapidly compressed (air) gas bubbles is evaluated.

SCE's adiabatic compression sensitivity test apparatus shown in Figure 1, is similar to the Bureau of Explosives compression apparatus (Refer to Figure 2) and the NAVORD OD 44811 adiabatic sensitivity test machine. This apparatus was designed to simulate conditions which might occur in an actual propellant line, and incorporates a device for applying pressure very rapidly to a gas bubble in contact with the liquid is rapidly compressed using a known drop weight system. Drop heights are varied to change the ignition conditions. The 50% point determination is calculated from the following equation:

$$50\%\ \text{Point} = (\text{lowest normalized height}) + (\text{log interval})\ (\sum AN/\sum N \pm 1/2)$$

The instantaneous compression in the chamber is measured by a pressure transducer. Since the pressure rise in the test chamber is rapid (10,000 - 1,000,000 psi/sec), the compression will be nearly adiabatic and rapid temperature rise will result.

The results of adiabatic compression sensitivity testing for nitromethane, nitro ethane and a propyl nitrate are show in Table III. Note, that the valves of 50% fire point of nitromethane and propyl nitrate are nearly identical to those determined at the United States Bureau of Mines previously. Calculations were made to determine energy/liquid volume and compression power.

HAZARD EVALUATIONS

From the initiation threshold data, one can determine the safety margin of liquid/slurry pumps. An example of several diaphragm pumps in-process potential was given. The comparisons for both energy/volume and compression power are show in Tables IV and V.

The propyl nitrate can initiate if a vapor or air bubble is present in pumps B and C and is marginal in Pump A. Nitromethane and nitro ethane appear to be safe in Pump A and somewhat marginal in Pumps B and C.

The compression power of the 3 pumps is all well below initiation thresholds. The check valve energy valves are considerably above the initiation threshold of all 3 fluids. Thus, the fluids should not be used in those diaphragm pumps with check valves.

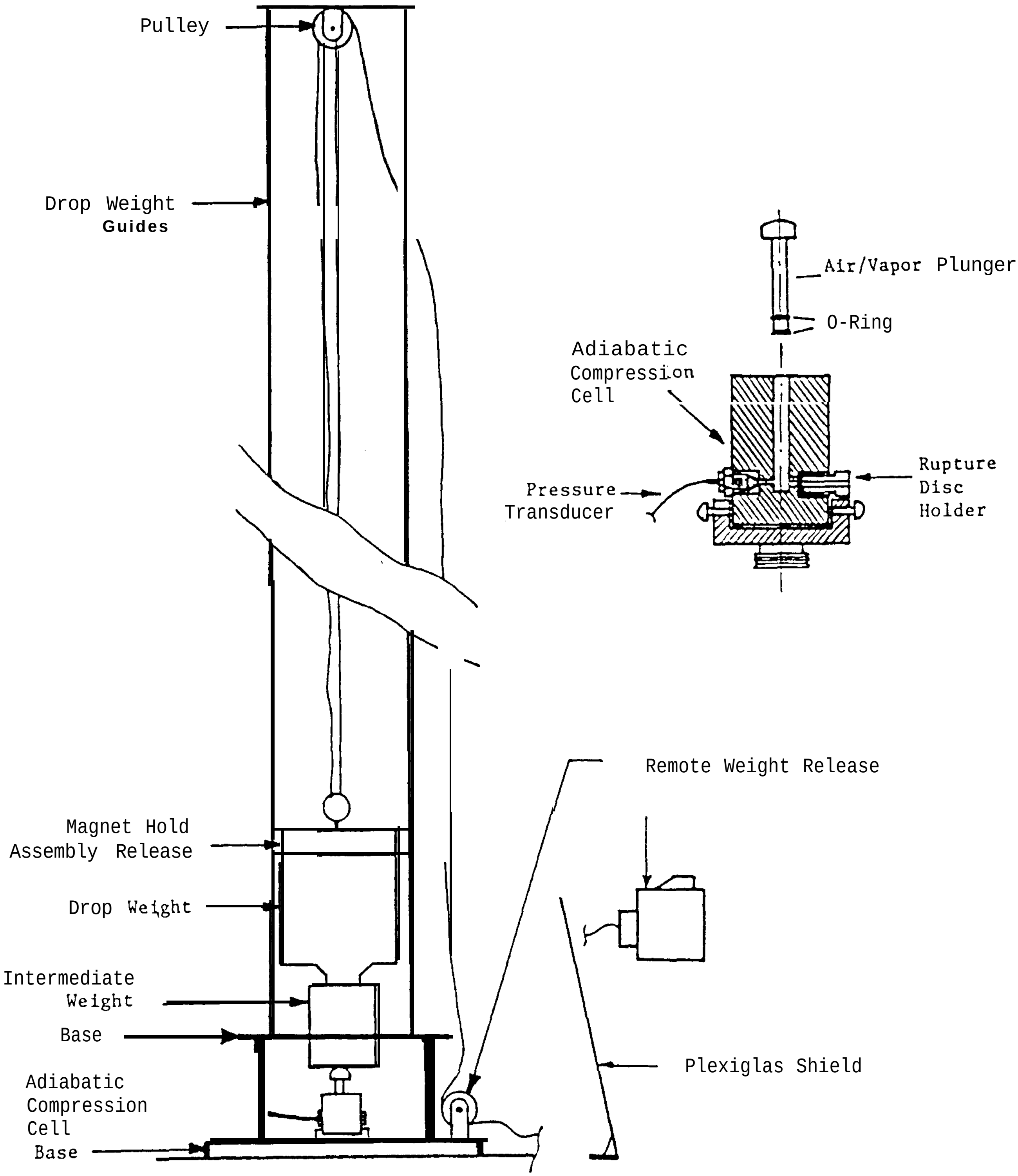

Figure 1. Adiabatic compression sensitivity tester setup with impact tester.

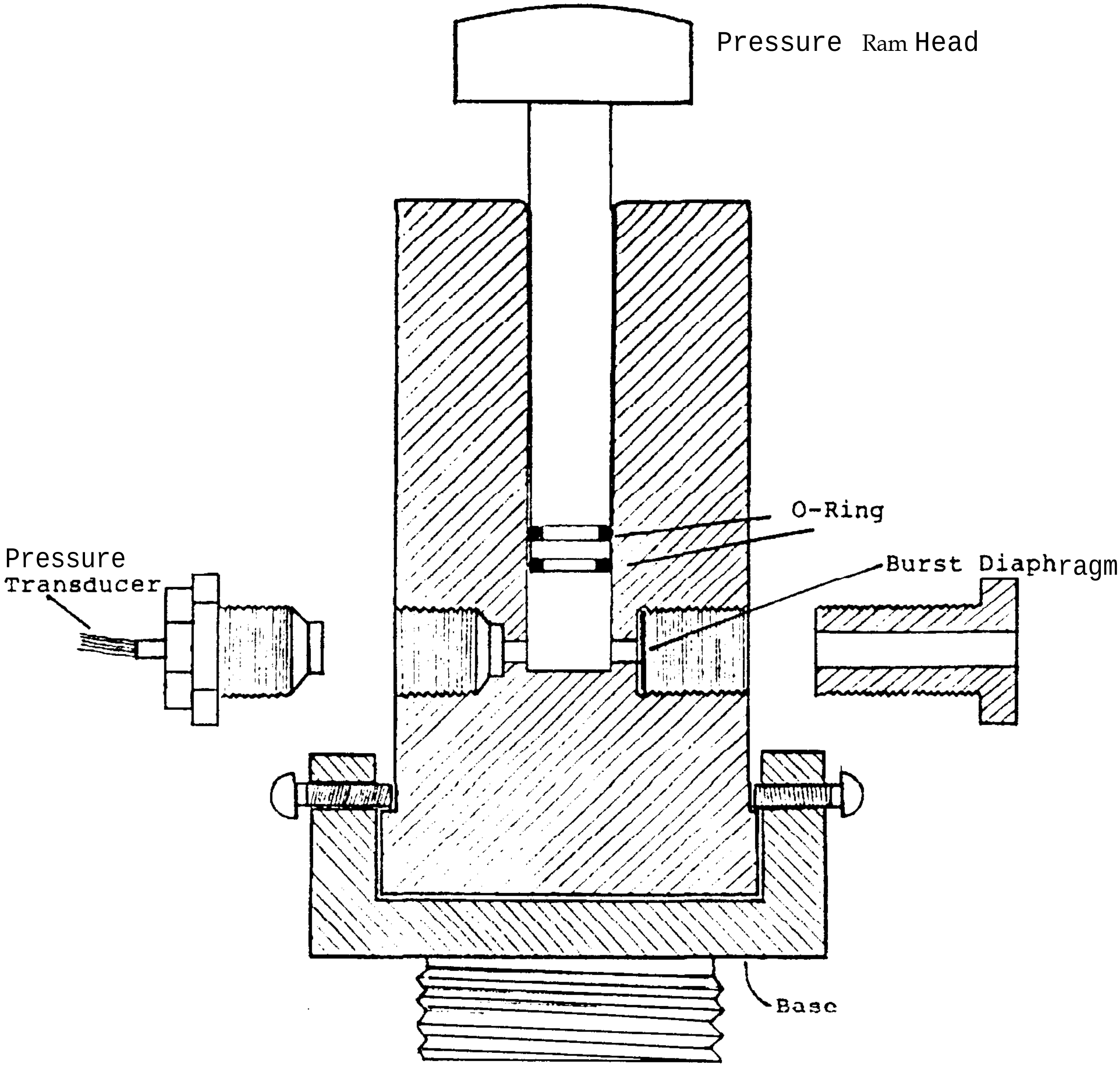

Figure 2. Compression Test Apparatus - Bureau of Explosives using Impact Tester.

TABLE III

ADIABATIC COMPRESSION INITIATION

SENSITIVITY OF VARIOUS MATERIALS

AT VOLUME RATIO - 25 $(T_f = 1900^0 F)$

Material	50% Fire Point H-(cm)	Mgh Energy (Joule)	(Kg-cm)	Engery Per time (J/sec)	Energy/Time Per Volume of Compression (J/sec-m^3)	Energy Per Volume Compression (J/m^3)
Nitromethane	23(24.2)*	11.28	1.15	948	524 x 10^6	6 x 10^6
Nitro Ethane	37	18.15	1.85	1925	1006 x 10^6	10 x 10^6
N Propylnitrate	4 (4)*	1.96	0.2	68	38 x 10^6	1 x 10^6

* US Bureau of Mines
Test Results

TABLE IV

COMPARISON OF IN PROCESS POTENTIALS

ENERGY/VOLUME WITH INITIATION THRESHOLDS

CHARACTERISTIC	PUMP (A)	PUMP (B)	PUMP (C)
1. Energy to Liquid in Pump (J/m^3)	0.44×10^6	1.3×10^6	1.71×10^6
2. Initiation Threshold (J/m^3)			
- Nirtomethane	6×10^6	6×10^6	6×10^6
- Nitro Ethane	10×10^6	10×10^6	10×10^6
- Propyl Nitrate	1×10^6	1×10^6	1×10^6

TABLE V

COMPARISON OF IN PROCESS POTENTIALS

COMPRESSION POWER TO INITIATION THRESHOLDS

CHARACTERISTIC	PUMP (A)	PUMP (B)	PUMP (C)
1. Compression Power (J/m^3 - sec)	26×10^6	60×10^6	66×10^6
2. Initiation Threshold (J/m^3 -sec)			
- Nirtomethane	524×10^6	524×10^6	524×10^6
- Nitro Ethane	1006×10^6	1006×10^6	1006×10^6
- Propyl Nitrate	38×10^6	38×10^6	38×10^6

CONCLUSIONS

From the above analysis, one can evaluate the potential of liquid/slurry initiation due to adiabatic compression in pumps. Knowing the pump characteristics, energy/volume of liquid and compression power, safety margins can be calculated from adiabatic compression testing initiation thresholds of energy/volume and compression power. From this analysis, risk assessment can be made for the pumping process.